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Uranium and thorium in Paleozoic rhyolites of Nova Scotia

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The concentrations of U and Th in Paleozoic rhyolites of Nova Scotia are closely related to their contents of K. The rhyolites were affected by secondary processes including low-grade metamorphism that could lead either to enrichment or depletion of these elements. The average abundances of U (ppm), Th (ppm), and K (%) in rhyolites are: Cambrian—2.69, 9.77, and 2.58, respectively; Silurian—4.50, 17.3, and 4.09, respectively; and Devono-Carboniferous—4.64, 18.3, and 5.67, respectively. The depletion of U, Th, and K in Cambrian rocks compared with younger Paleozoic rhyolites is probably related to secondary processes. In Silurian and Devono-Carboniferous rhyolites, these elements were mainly redistributed during the secondary processes, but not removed.

Les concentrations en U et Th des rhyolites paléozoïques de la Nouvelle-Écosse sont en relation étroite avec les teneurs en K. Les rhyolites ont été affectées par des processus d'altération secondaire, incluant un métamorphisme de faible intensité, qui ont pu produire soit un enrichissement ou un appauvrissement de ces éléments. Les teneurs moyennes en U (ppm), Th (ppm) et K (%) dans les rhyolites sont: cambriennes—2,69, 9,77 et 2,58 respectivement, siluriennes—4,50, 17,3 et 4,09 respectivement et dévono-carbonifères—4,64, 18,3 et 5,67 respectivement. L'appauvrissement des éléments U, Th et K dans les roches cambriennes par rapport aux roches paléozoïques plus récentes est probablement relié aux processus d'altération secondaire. Dans les rhyolites siluriennes et dévono-carbonifères, ces éléments furent principalement redistribués durant les processus d'altération secondaire, sans occasionner la perte de ces éléments.

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Introduction

Silicic volcanic rocks and tuffs have frequently been considered to be a primary source of uranium for many deposits (e.g., Devoto 1978). Although the behaviour of U during magmatic processes and in fresh volcanic rocks is relatively well established (Locardi 1967; Rogers and Adams 1969*a*,*b*; Dostal *et al.* 1976), there is only a limited amount of information on the distribution and variation of U in silicic volcanic rocks affected by secondary processes such as low-grade metamorphism. The purpose of this paper is to present some geochemical data, particularly on U and Th in the Paleozoic rhyolitic rocks of Nova Scotia that were subjected to low-grade regional metamorphism. The age of these volcanic rocks ranges from Cambrian to Devono-Carboniferous.

Geological notes

Paleozoic volcanic rocks are widely distributed throughout Nova Scotia although their areal exposure is relatively limited. Their occurrence, petrography, and a preliminary geochemical study of basalts have been recently described by Keppie and Dostal (1980) and thus only a brief summary is given here.

The volcanic suites are of Early–Middle Cambrian, Late Ordovician – Early Silurian, and Middle Devonian – Early Carboniferous ages. They are usually bimodal, composed of rhyolites and basalts predominantly of tholeiitic affinities, although some basalts appear to be alkaline (Sarkar 1978). The volcanic rocks were probably extruded in tensional areas during transpression or rifting following the Cadomian, Taconian, and Acadian orogenic events. All these volcanic suites were affected to varying degrees by secondary alteration processes including subgreenschist, greenschist, and amphibolite facies metamorphism.

Volcanic rocks of Cambrian age crop out in southern Cape Breton Island and the Antigonish Highlands (Fig. 1). The Middle Cambrian Bourinot Group of Cape Breton Island forms a narrow belt 24 km long and 200–600 m thick. The main rock types are basalts, rhyolites, and tuffs interbedded with shallow-marine sedimentary rocks (Helmstaedt and Tella 1973). Southeast of the Bras d'Or lakes equivalent rocks can be

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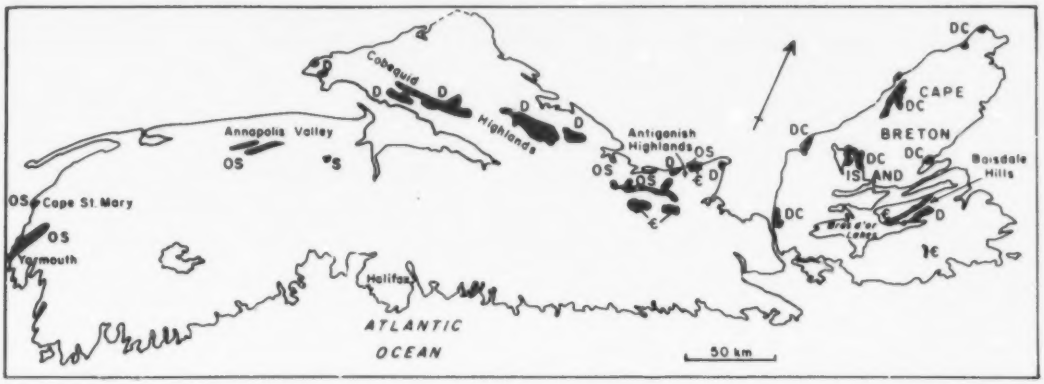

FIG. 1. Map showing the distribution of Paleozoic volcanic rocks in Nova Scotia (modified after Keppie and Dostal 1980): Cambrian (C), Late Ordovician–Silurian (OS), Devonian (D), and Devono-Carboniferous (DC).

followed for approximately 8 km and are 50–300 m in thickness. In the northern Antigonish Highlands, the Arbuckle Brook Group, which is 800 m thick, is exposed in an area of at least 5 km^2. It is formed by subaerial to submarine rhyolitic and basaltic flows and tuffs that are interbedded with a subordinate amount of sedimentary rocks (Murphy *et al.* 1979). Both these Cambrian sequences were metamorphosed under greenschist facies grade (Helmstaedt and Tella 1973; Murphy 1982) and only rarely are original magmatic minerals preserved.

The volcanics of Late Silurian to Early Devonian age were collected from the Annapolis Valley and the Antigonish Highlands. In the Annapolis Valley, a volcanic sequence composed of subaerial to shallow-marine basalts and rhyolites forms part of the Silurian White Rock Formation, and was affected by greenschist facies grade metamorphism, which replaced most of the magmatic mineral assemblage. The basalts are up to 30 m thick and crop out over a distance of approximately 40 km, and the rhyolites vary from 10 to 50 m in thickness and are exposed for about 25 km (Smitheringale 1973). The volcanic rocks of the Antigonish Highlands exposed between Arisaig Pier and Dunn Point have been divided into two groups: the Dunn Point and McGillivray Brook Formations (Boucot *et al.* 1974; Keppie *et al.* 1978*b*), covering 2 km × 0.25 km in area. The Dunn Point Formation is more than 220 m thick and consists of basalts and rhyolites. The McGillivray Brook Formation mainly contains ignimbrites as well as rhyolites and lahars. It is up to 130 m thick and conformably overlies the Dunn Point rocks. Both suites were also metamorphosed to greenschist facies grade (Keppie *et al.* 1978*b*) and primary magmatic mineral phases show moderate extent of replacement by secondary minerals.

Devono-Carboniferous volcanic rocks were collected from three regions: Cape Breton Island, Cobequid Highlands, and northern Antigonish Highlands. The volcanic rocks of the Upper Devonian – Lower Carboniferous Fisset Brook Formation occur intermittently along the northwestern shore of Cape Breton Island (Kelley and MacKasey 1964; Blanchard 1982). The formation, which ranges from 250 to 1000 m in thickness, consists predominantly of basalts and rhyolites that are intercalated with sedimentary rocks. They underwent mainly incipient alteration and subgreenschist facies metamorphism (Smith and Macdonald 1981), and original magmatic minerals are largely preserved. Similar occurrences of basalts and rhyolites are present throughout the Cobequid Highlands and are considered to be both Devonian and Carboniferous (Donohoe and Wallace 1978). Some rhyolites were also collected from Wilkie Brook in the northern Antigonish Highlands (Keppie *et al.* 1978*a*). These rocks, from a section 100 m thick, are possibly equivalent to the Fisset Brook Formation. Both Cobequid Highlands and Wilkie Brook suites suffered incipient alteration and subgreenschist facies metamorphism.

Petrography

The rhyolites are typically porphyritic, composed of quartz and feldspar phenocrysts set in a devitrified glassy or fine-grained matrix. They have been affected by secondary processes (as previously described), which have modified the mineralogy to varying degrees. The products of alteration include common occurrences of albite, epidote, sericite, calcite, prehnite, hematite, biotite, and clay minerals (Benson 1974; Boucot *et al.* 1974; Cameron 1980; Kelley and MacKasey 1964; Keppie and Dostal 1980; Keppie *et al.* 1978*b*). The

TABLE 1. Chemical composition of representative

	Cambrian									
	Bourniot Group						Arbuckle Brook Group			
	1	2	3	4	5	6	7	8	9	10
SiO_2 (%)	68.72	69.55	74.85	70.00	72.60	78.10	69.50	73.10	78.39	68.82
Al_2O_3	14.63	7.74	12.47	14.50	14.70	10.20	14.70	13.40	10.65	15.21
Fe_2O_3	3.68	5.96	2.91	2.11	1.70	3.28	2.68	2.04	0.75	1.13
FeO	1.22	6.85	1.07	0.25	0.25	0.50	1.80	0.70	1.36	2.23
MnO	0.06	0.09	0.04	0.04	0.01	0.05	0.20	0.28	0.05	0.04
MgO	1.44	1.54	1.02	0.26	0.37	0.28	0.91	0.54	0.68	1.00
CaO	0.53	0.69	0.40	1.87	0.40	1.15	1.83	0.87	0.75	0.99
Na_2O	6.06	0.64	5.56	4.94	5.17	1.79	1.97	4.75	2.84	5.83
K_2O	0.98	1.34	0.55	3.90	2.42	3.45	2.02	2.02	2.91	2.54
TiO_2	0.28	0.87	0.52	0.41	0.50	0.22	0.32	0.72	0.28	0.53
P_2O_5	0.04	0.38	0.04	0.06	0.08	0.01	0.09	0.09	0.09	0.14
H_2O^+	1.52	3.45	1.22	0.15	0.50	0.40	2.55	1.00	1.32	1.97
H_2O^-	0.08	0.16	0.09	1.61	0.92	0.72	1.60	0.60	0.24	0.50
Li (ppm)							25	7	9	11
Rb	40	46	28	82	83	137	53	60	81	74
Sr	322			92	103	176	128	194		
Ba	289	152	208	378	254	841	781	490		
Zr	577			254	374	817	207	245		
Nb	27	10	22	15	18	30	14	14	12	15
La	28	31	34	18	22	37	40	33		
Ce	72	92	80	41	63	98	81	70		
U	2.6	0.8	1.9	2.5	3.1	3.2	2.3	2.7	2.2	3.3
Th	12	3	9	15	11	10	8	8	9	13

NOTES: Sample numbers refer to material housed in the collection of the Nova Scotia Department of Mines and Energy. Samples 4, 5, and 6 taken from Cameron (1980). 1 = F15-6023; 2 = F15-6025; 3 = F15-6062; 4 = KJC-14; 5 = KJC-24; 6 = KJC-49; 7 = E16-304; 8 = E16-472; 9 = E16-811; 10 = E16-813; 11 = A14-6003; 12 = A14-6005; 13 = A14-6013; 14 = E16-6014; 15 = E16-6024; 16 = E16-6034; 17 = NO2-1216; 18 = KO3-0003; 19 = F13-6042A; 20 = F13-6044B; 21 = F13-6043; 22 = HO8-4447; 23 = HO8-4448.

ignimbrites collected from the McGillivray Brook Formation are generally compact eutaxitic welded tuffs made up of devitrified glass shards, embayed quartz crystals, and pumice fragments enclosed in a quartz–feldspar groundmass. The primary mineral assemblages are partly or completely replaced by albite, epidote, sericite, calcite, and clay minerals (Boucot *et al.* 1974; Keppie *et al.* 1978*b*). The Paleozoic volcanic rocks usually show little deformation. Exceptions are some rocks of the Arbuckle Brook Group, which were affected by a penetrative cleavage.

Analytical notes

The major-element analyses were done either by wet methods at the Technical University of Nova Scotia or by X-ray fluorescence and supplementary techniques at X-Ray Assay Laboratories Ltd., Toronto. The trace elements Rb, Sr, Ba, Zr, Nb, La, and Ce were determined by X-ray fluorescence, whereas Li was analyzed by atomic absorption. The precision and accuracy of these determinations have been given by Dupuy *et al.* (1979). In general, the precision of these trace elements is better than 10%. The major elements and Rb, Sr, Ba, Zr, Nb, La, and Ce data for seven samples from the Bourinot suite were previously reported by Cameron (1980). U and Th were determined in 61 samples at X-Ray Assay Laboratories Ltd., Toronto by delayed and instrumental neutron activation methods, respectively. Four replicate analyses of one rhyolite sample give U contents of 4.75 ± 0.24 ppm ($\pm 1\sigma$) and Th values of 20.5 ± 1.0 ppm ($\pm 1\sigma$). The precision is generally considered to be less with rocks containing less than 2 ppm of U and 10 ppm of Th. The individual chemical analyses and locations of the samples are deposited in the Open File Library of the Nova Scotia Department of Mines and Energy (OF 523: Chemical analyses of Paleozoic rhyolites in Nova Scotia).

Major-element geochemistry

Major- and trace-element analyses of representative samples of rhyolitic rocks (selected from 61 analyzed

Paleozoic rhyolitic rocks from Nova Scotia

Late Ordovician – Silurian						Devonian and Devono-Carboniferous						
White Rock Group			Dunn Point Group	McGillivray Brook Group		Fisset Brook Group		Wilkie Brook Group			Cobequid Highlands	
11	12	13	14	15	16	17	18	19	20	21	22	23
74.28	74.64	71.33	77.86	75.39	82.34	74.90	70.79	73.82	76.85	75.43	75.62	73.35
12.56	13.70	15.49	11.71	10.58	9.96	11.70	14.24	11.81	10.34	10.93	13.50	13.63
2.31	0.36	2.29	2.10	2.50	1.23	2.24	0.45	1.89	0.75	2.38	0.00	0.86
1.57	1.10	0.45	0.65	0.40	0.45	0.85	1.45	0.32	0.30	0.39	2.76	0.67
0.04	0.04	0.00	0.01	0.01	0.01	0.05	0.03	0.01	0.01	0.02	0.02	0.01
0.94	0.85	0.12	0.11	0.13	0.19	0.11	0.50	0.73	0.73	1.42	0.36	0.17
0.79	1.48	0.30	0.34	0.35	0.15	0.63	0.14	0.36	0.27	0.42	0.64	0.21
3.72	0.84	4.41	3.80	0.34	0.26	2.03	1.57	0.95	0.37	1.30	4.19	2.15
1.88	3.94	5.87	3.08	7.13	3.52	6.60	9.18	7.14	6.78	3.12	3.20	7.94
0.49	0.23	0.24	0.18	0.16	0.20	0.28	0.30	0.23	0.15	0.27	0.20	0.18
0.42	0.28	0.02	0.03	0.03	0.03	0.02	0.04	0.05	0.04	0.05	0.02	0.03
1.22	1.64	0.74	0.53	0.48	1.50	0.40	0.79	1.84	1.19	2.94	1.19	0.69
0.15	0.41	0.21	0.15	0.15	0.33	0.37	0.17	0.80	0.54	0.88	0.25	0.00
15	40	5	4	3	7	9	9	22	41	54		
106	149	173	107	293	167	143	293	190	229	99	122	198
177	121	132	126	103	108	70	103	33	13		292	197
190	227	2281	1178	3246	5179	297	1457				274	534
128	121	543	450	1386	1122	689	211	784	607		228	216
15	15	58	46	99	66	35	15	44	43		23	24
17	17	41	67	78	86	129	26				54	33
42	40	81	161	165	151	274	47				113	69
4.0	4.3	4.3	4.8	8.3	2.1	4.1	7.7	4.8	8.8	7.0	3.6	4.0
6	8	24	20	30	18	20	25	24	23	23	16	13

rocks) are given in Table 1. The samples have been divided on the basis of age, regional distribution, and chemical composition into eight groups: two groups of Cambrian age (Bourinot and Arbuckle Brook), three of Silurian age (Dunn Point, McGillivray Brook, and White Rock), and three of Devono-Carboniferous age (Cobequid, Wilkie Brook, and Fisset Brook). Most rocks have SiO_2 contents ranging between 70 and 76%. A few samples from various groups contain less than 70% SiO_2; samples with $SiO_2 > 76\%$ are mainly from the McGillivray Brook Formation. The low-SiO_2 (<70%) rocks have relatively high Ti, Fe, Mg, and Ca contents as well as the petrography typical of dacites. The majority of samples contain >11% of Al_2O_3 and have a peraluminous character and normative corundum. With the exception of two low-SiO_2 samples, the rocks contain more than 80% normative quartz and feldspars. However, there are wide variations in chemical composition among the rocks of individual groups and also to a smaller extent between groups.

The Cambrian volcanic rocks display the largest range of compositional variations, particularly of K_2O and Na_2O. These variations are also reflected by the wide scatter of normative compositions of the rocks on the Ab–Or–Q ternary diagram (Fig. 2). Bourinot rhyolites have, in general, the lowest K_2O but the highest Na_2O contents among the studied Paleozoic volcanics (Table 2). A few samples of the Bourinot Group plot in the granitic field of Winkler and Von Platen (1961) on the Ab–Or–Q diagram (Fig. 2). Most Bourinot volcanics, however, fall outside the granitic field and are displaced toward either the Ab or Q apex on the diagram. They are usually low in CaO (<1%). Samples that are close to the Ab corner are not only strongly enriched in Na_2O (up to 5–6%) but are also depleted in K_2O (frequently <1%). Rocks that extend toward the Q apex on the Ab–Or–Q diagram are either enriched in SiO_2 (>76%, e.g., sample 6 in Table 1) or depleted in both Na_2O and K_2O. The strong depletion in alkalies is usually accompanied by strong Fe enrichment and Al depletion (e.g., sample 2 in Table 1).

The rhyolites from the Arbuckle Brook Group are, in general, similar to the Bourinot rocks, particularly in the large chemical variations and scatter of data on the Ab–Or–Q ternary plot. However, they are usually lower in Na_2O (Table 2).

The volcanic rocks of the Silurian White Rock Formation have on average higher SiO_2 and lower total

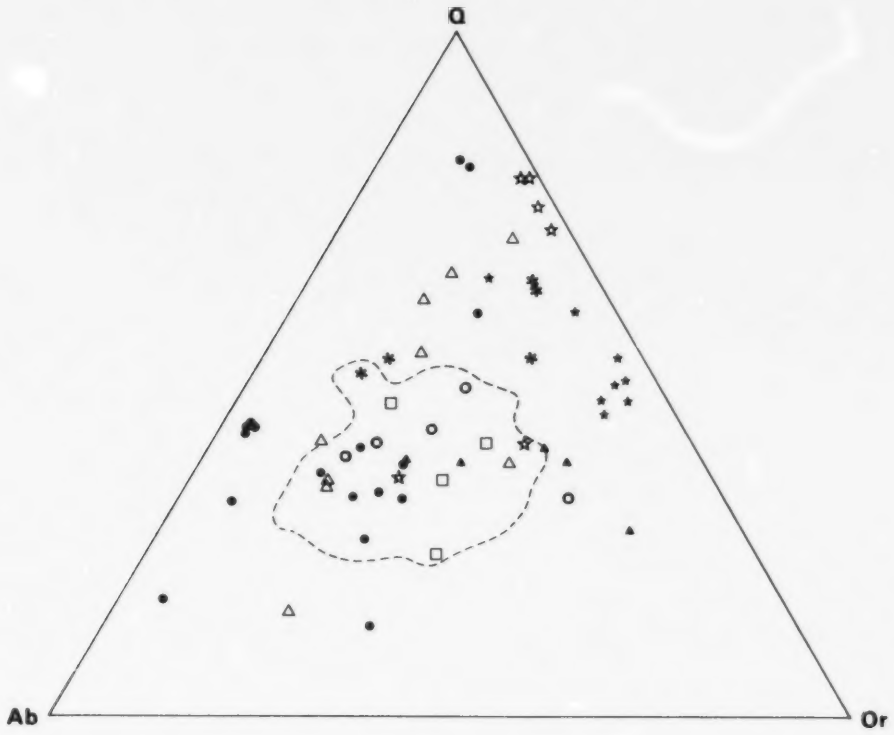

FIG. 2. Ab–Or–Q ternary projection of normative compositions of acidic volcanic rocks. Solid lines enclose analyses of 1190 granitic rocks (Winkler and Von Platen 1961). Cambrian: ● = Bourinot; △ = Arbuckle Brook. Late Ordovician – Silurian: * = White Rock; □ = Dunn Point; ☆ = McGillivray Brook. Devonian and Devono-Carboniferous: ▲ = Fisset Brook; ★ = Wilkie Brook; ○ = Cobequid Highlands.

alkalies, particularly Na_2O, than the Cambrian rhyolites. On the Ab–Or–Q diagram (Fig. 2), most of the White Rock samples plot outside the granitic field, towards the Q apex. The rhyolites of the Dunn Point Formation resemble equivalent recent rocks in their major-element composition (e.g., Bacon *et al.* 1981; Crecraft *et al.* 1981) and fall into the granitic field on the normative Ab–Or–Q diagram. The rocks from the nearby McGillivray Brook Formation have higher SiO_2 but distinctly lower Na_2O contents (Table 2) and on the Ab–Or–Q diagram they are displaced towards the Q apex, outside the granitic field. The rhyolites of both the Dunn Point and McGillivray Brook Groups are generally lower in CaO and MgO than the other analyzed rhyolites. Compared with samples of the Dunn Point Formation that represent lava flows, the analyzed rocks of the McGillivray Brook Formation are mostly ignimbrites.

The rhyolites of both the Devono-Carboniferous Fisset Brook Formation and equivalents in Wilkie Brook are strongly enriched in K_2O (Table 2) relative to equivalent recent rocks (e.g., Bacon *et al.* 1981; Mahood 1981) and the other analyzed Paleozoic rhyolites. Those from Wilkie Brook are composed of rocks with a relatively homogeneous composition characterized by low Na contents. The Fisset Brook rhyolites show a wide variation of alkalies marked by a negative correlation of K_2O with Na_2O. On the Ab–Or–Q diagram (Fig. 2), the Wilkie Brook rhyolites form a distinct cluster along the Q–Or join. On the other hand, the rhyolites of the Fisset Brook Formation are scattered on this plot but display a trend from the region of the thermal minimum towards the Q apex. Devono-Carboniferous silicic rocks of the Cobequid Highlands have highly variable chemical compositions and are dispersed on the Ab–Or–Q diagram although most of them lie within the granitic field.

The composition of many rhyolites differs significantly from that of equivalent fresh volcanic rocks, and the ranges of chemical variations within individual groups are generally larger than those observed in suites of recent rhyolitic rocks. The large major-element

TABLE 2. Average contents of U, Th, K_2O, and Na_2O in Paleozoic rhyolites

	U (ppm)	Th (ppm)	K_2O (%)	Na_2O (%)	Th/U	10^4 U/K	10^4 Th/K	No. of samples
Cambrian								
Bourinot	2.64 (1.05)	9.76 (2.63)	2.29 (1.57)	4.47 (1.86)	3.7	1.4	5.1	17
Arbuckle Brook	2.74 (1.15)	9.78 (4.38)	2.86 (1.08)	3.47 (2.03)	3.6	1.2	4.1	9
Late Ordovician – Silurian								
White Rock	3.98 (0.60)	7.40 (0.89)	3.16 (1.00)	1.94 (1.38)	1.8	1.5	2.8	5
Dunn Point	4.30 (0.56)	20.4 (2.07)	4.73 (1.08)	3.73 (0.61)	4.7	1.1	5.2	5
McGillivray Brook	5.23 (3.15)	24.0 (9.80)	4.37 (1.84)	0.62 (0.84)	4.6	1.4	6.6	6
Devonian and Devono-Carboniferous								
Fisset Brook	5.24 (1.76)	21.0 (4.53)	6.29 (2.24)	2.38 (0.77)	4.0	1.0	4.0	5
Wilkie Brook	5.41 (1.66)	23.4 (1.92)	6.28 (1.45)	0.71 (0.31)	4.3	1.0	4.5	8
Cobequid Highlands	3.25 (1.41)	10.4 (5.9)	4.44 (2.00)	2.64 (1.47)	3.2	0.89	2.8	6

NOTE: Values in brackets correspond to one standard deviation (1σ).

variations (including the scatter on the normative Ab–Or–Q diagram) and the mineralogical evidence indicate that many major elements, particularly K and Na, have been affected to a variable degree by secondary processes including low-grade metamorphism. However, the element remobilization was not uniform among the analyzed rocks. Four types of compositional variation trends have been distinguished. The first type is characterized by Na enrichment, which is accompanied by the progressive depletion of K. On the Ab–Or–Q diagram, the trend produced displacement towards the Ab apex. The second trend leads to K enrichment associated with the depletion of Na, particularly marked in the rhyolites from Wilkie Brook. The other two types are characterized by displacement towards the Q apex on the Ab–Or–Q diagram. This relative enrichment of normative quartz relative to feldspars can be due either to enrichment in SiO_2 or to depletion of alkalies. When the depletion in alkalies is severe, it is accompanied not only by impoverishment in Al but also by Fe enrichment. However, contrary to the anomalously high abundances of SiO_2 in some rocks of the McGillivray Brook Formation, the low SiO_2 content (particularly <70%) accompanied by high Fe, Mg, and Ca observed in several rocks with the petrographic features of dacites is due to magmatic processes.

Trace-element geochemistry

The silicic volcanic rocks display a wide range of distributions of incompatible trace elements. Several elements such as Rb and U, which are generally considered to be mobile during secondary processes, usually show, like Th, a positive correlation with K (Fig. 3). Other elements including Zr, Nb, La, and Ce, which are relatively immobile, seem to have a complex relationship with the major elements. In general, they do not correlate with the major elements, although such a relationship is occasionally shown by some rocks from a particular area. For example, several rhyolites from the Fisset Brook Formation, which contain 8–10% K_2O, are depleted in these elements, whereas high-SiO_2 rocks of the McGillivray Brook Formation have very large concentrations of Zr, Nb, La, and Ce. These trace elements show good positive correlation among themselves but do not usually have a clear relationship with mobile trace elements (Fig. 4). The abundances of Li seem to be related to the amount of ferromagnesian minerals, as indicated by a positive correlation of Mg with Li. There is no obvious relationship between Li and K or Na.

Both Devono-Carboniferous groups (Wilkie Brook and Fisset Brook) display K enrichment trends. In the rhyolites of the Fisset Brook Formation, K correlates positively with Rb, Th, and U, whereas Na has an inverse relationship with these elements. U and Th in the rocks of the Fisset Brook Formation show a distinct positive correlation (+0.78; Fig. 5). On the other hand, La, Ce, Zr, and Nb do not relate to the major elements including K and Na. Samples enriched in K generally have the highest K/Rb and Rb/Sr ratios. The increase of K leads, however, to only a slight increase of the Th/U ratio and does not affect the U/K ratio.

The rocks from Wilkie Brook have K_2O contents similar to those of Fisset Brook rhyolites but they have on average significantly lower Na_2O contents (Table 2). The differences in Na_2O do not affect the contents of Rb, U, and Th, which like K_2O are high and comparable in both regions. It seems that the abundances of Rb, U, and Th are related to K.

The rhyolites of the Bourinot Group display large compositional variations with two enrichment trends. The first one has an enrichment of Na and the second is characterized by a depletion in both K_2O and Na_2O. The increase of Na is accompanied by an increase in Th but a

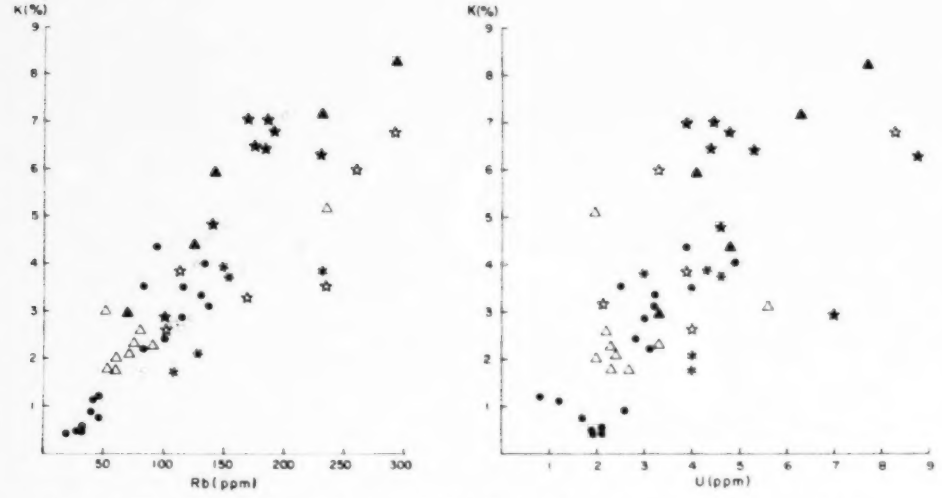

FIG. 3. Variations of K vs. Rb and K vs. U in Paleozoic rhyolites of Nova Scotia. The symbols are the same as in Fig. 2.

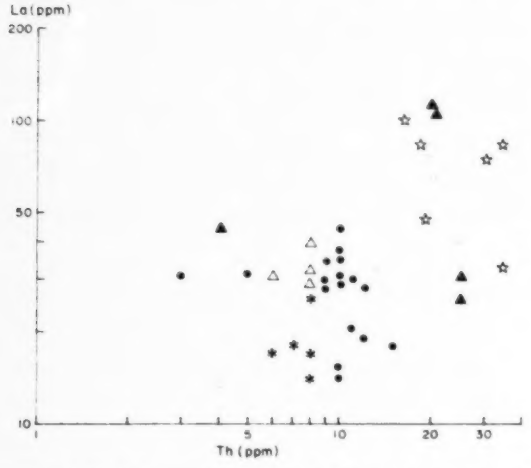

FIG. 4. Variations of La vs. Th in Paleozoic rhyolites of Nova Scotia. The symbols are the same as in Fig. 2.

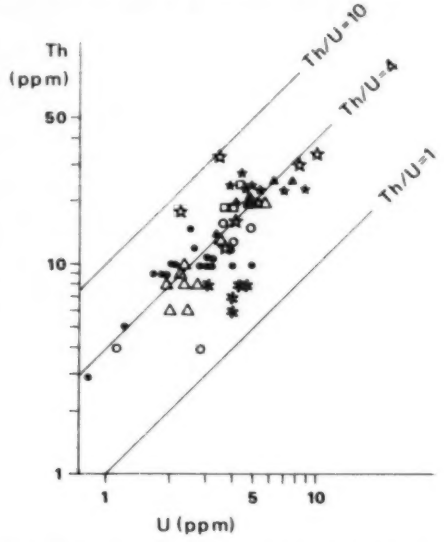

FIG. 5. Variations of U vs. Th in Paleozoic rhyolites of Nova Scotia. The symbols are the same as in Fig. 2.

decrease of K, Rb, and U. Samples enriched in Na and depleted in K have very high Th/K and U/K and low K/Rb ratios. Although Rb and U show a positive correlation with K, the elements differ in the degree of their relative depletion with K being the most depleted and U the least depleted elements during the Na enrichment process. The close coherence of U and Th has also been affected and these two elements show only a relatively weak positive correlation. The second trend (depletion of Na_2O and K_2O) is accompanied by depletion of Th, U, Rb, and Ba while their corresponding ratios remain unchanged. Sr in the Bourinot Group shows a strong negative correlation with K (−0.81) and Rb (−0.77). In fact, the high-K_2O rhyolites from the other areas are strongly depleted in Sr.

The trend of SiO_2 enrichment as represented by samples from the McGillivray Brook Formation with a very high content of SiO_2 (78–82%) is characterized by high contents of La, Ce, Zr, and Nb. This process does not seem to significantly change the abundances of Rb, U, and Th, which are closely related to K. Likewise the element ratios among these mobile elements appear not to be affected by the SiO_2 variations.

Discussion

The Paleozoic rhyolites have been subjected to secondary processes, which in many rocks have had a pronounced effect on the mineralogy and the contents of alkalies. A wide distribution of alkalies, their strong impoverishment associated with the depletion of Al and enrichment of Fe, and a distinct K enrichment (8–10%) accompanied by strong Na depletion are not readily compatible with magmatic processes. Likewise, the significant scatter of the normative composition of rhyolites on the Ab–Or–Q ternary projection provides additional evidence of the effect of the secondary processes on chemistry.

The close relationship of U and Th with alkalies in the rhyolites and the absence of their correlation with rather immobile trace elements such as Zr, Nb, La, and Ce suggest that the distribution of U and Th in the studied rocks is mainly determined by secondary processes, probably by low-grade metamorphism, and that the bulk of the radioactive elements is not concentrated in accessory minerals.

A histogram of uranium concentrations (Fig. 6) shows a frequency distribution skewed toward the higher values, with a mean of 3.74 ± 1.84 ppm (±1σ). Comparison with the histogram of U contents of silicic igneous rocks given by Rogers and Adams (1969a) indicates that the Paleozoic rhyolites have a range similar to that for the entire silicic igneous population, although their mode is higher and the distribution is more skewed. The rocks with high U contents have typically high K_2O and very low Na_2O/K_2O ratios. A histogram of Th abundances in the rhyolitic rocks (Fig. 6) displays two areas of high frequency, with one maximum in the range of 8–10 ppm and the other in the range of 22–26 ppm. The samples with high Th are generally either enriched in K or Na, further indicating an important role of secondary processes in the distribution of this element. The mean of the Th values is 14.24 ± 7.84 ppm (±1σ). Despite the large range of variation, the average value for the Th/U ratio (3.8) is closely comparable to the average Th/U ratio for igneous rocks in general, which is in the range of 3.5–4 (Rogers and Adams 1969*a*). Likewise, the average $10^4 \times U/K$ and $10^4 \times Th/K$ ratios (1.16 and 4.44, respectively) are comparable to the averages of these ratios in rhyolitic and granitic rocks (Cheminee 1970).

Several studies (e.g., Rosholt *et al.* 1973; Rogers *et al.* 1965) have indicated that U could be lost during weathering. However, similarities between the average Th/U and U/K ratios and the typical average values for recent fresh equivalent rocks (e.g., Cheminee 1970) suggest that the Paleozoic rhyolites, in general, did not lose a significant amount of U during weathering.

The average abundances of U, Th, and K from the individual areas display distinct differences. The

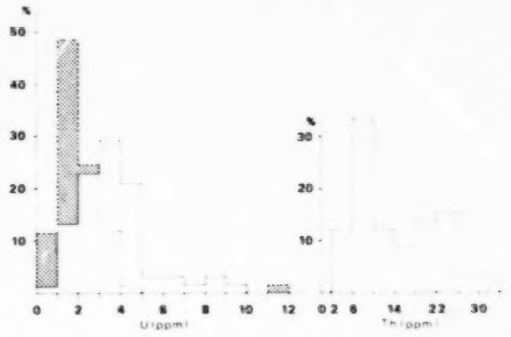

FIG. 6. Histogram of uranium and thorium concentrations in Paleozoic silicic volcanics of Nova Scotia (number of samples = 61). Histogram of U in silicic igneous rocks compiled by Rogers and Adams (1969*b*) is shown for comparison (dotted area enclosed by dashed line).

Cambrian rhyolites are lower in U and Th and also K and Rb than Silurian and Devono-Carboniferous rocks. The average contents of U and Th in the Bourinot and Arbuckle Brook Groups (Table 2) are lower than the averages for rhyolitic and granitic rocks given by Rogers and Adams (1969*a*,*b*) as 5 ppm U and 18 ppm Th, or the recent fresh silicic extrusive rocks (Mahood 1981; Crecraft *et al.* 1981). As the Cambrian rhyolites are the most intensely affected by secondary processes among the analyzed rocks, it suggests that the depletion of U and Th (and also K and Rb) is due to their removal during alteration and does not reflect primary magmatic abundances. On the other hand, several other areas seem to have average U and Th contents comparable to the averages given for rhyolitic and granitic rocks, indicating that the rocks probably did not suffer significant loss of these elements although U and Th probably have been redistributed. Exceptions are the White Rock rhyolites, which are depleted in Th. The enrichment of rhyolites in U and Th is clearly associated with the increase of K, whereas their depletion is usually related to the impoverishment of rhyolites in alkalies (both K and Na). A distinct increase of Na in some rhyolites is accompanied by the enrichment of Th and decrease of K, Rb, and U.

Conclusion

The abundances of U and Th in Paleozoic rhyolites from Nova Scotia are related to their contents of K. Their distribution is strongly affected by secondary (probably low-grade metamorphic) processes, which could lead either to their enrichment or depletion. Cambrian silicic volcanic rocks are depleted in U, Th, and K relative to younger Paleozoic rhyolites. This difference is probably also related to the secondary processes. On the other hand, the average U and Th

abundances of Silurian and Devono-Carboniferous rhyolites are comparable to the averages given by Rogers and Adams (1969*a*,*b*) and Cheminee (1970) for rhyolitic and granitic rocks, suggesting that radioactive elements in these rocks are mainly redistributed (as also indicated by the large scatter of the values of U and Th) but not removed.

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BACON, C. R., MACDONALD, R., SMITH, R. L., and BAEDECKER, P. A. 1981. Pleistocene high-silica rhyolites of the Coso volcanic field, Inyo County, California. Journal of Geophysical Research, **86**, pp. 10 223 – 10 241.

BENSON, D. G. 1974. Geology of the Antigonish Highlands, Nova Scotia. Geological Survey of Canada, Memoir 376, 92 p.

BLANCHARD, M. C. 1982. Geochemistry and petrology of the Fisset Brook Formation, western Cape Breton, Nova Scotia. M.Sc. thesis, Dalhousie University, Halifax, N.S., 198 p.

BOUCOT, A. J., DEWEY, J. F., DINELEY, D. L., FLETCHER, R., FYSON, W. K., GRIFFIN, J. G., HICKOX, C. F., MCKERROW, W. S., and ZIEGLER, A. M. 1974. Geology of the Arisaig area, Antigonish County, Nova Scotia. Geological Society of America, Special Paper 139, 191 p.

CAMERON, K. J. 1980. Geochemistry of Cambrian volcanic rocks of the Bourinot Group, Cape Breton Island. B.Sc. thesis, Saint Mary's University, Halifax, N.S., 40 p.

CHEMINEE, J. L. 1970. Distribution de l'uranium, du thorium et du potassium dans les roches volcaniques de l'Afar septentrional (Ethiopie). Bulletin Volcanologique, **34**, pp. 168–195.

CRECRAFT, H. R., NASH, W. P., and EVANS, S. H., JR. 1981. Late Cenozoic volcanism at Twin Peaks, Utah: geology and petrology. Journal of Geophysical Research, **86**, pp. 10 393–10 320.

DEVOTO, R. H. 1978. Uranium in Phanerozoic sandstone and volcanic rocks. *In* Uranium deposits: their mineralogy and origin. Short course handbook. *Edited by* M. M. Kimberley. Mineralogical Association of Canada, University of Toronto Press, Toronto, Ont., pp. 293–306.

DONOHOE, H. V., JR., and WALLACE, P. I. 1978. Geology map of the Cobequid Highlands. Nova Scotia Department of Mines, Preliminary Map 78-1.

DOSTAL, J., CAPEDRI, S., and DUPUY, C. 1976. Uranium and potassium in calc-alkaline volcanic rocks from Sardinia. Lithos, **9**, pp. 179–183.

DUPUY, C., DOSTAL, J., and COULON C. 1979. Geochemistry and origin of andesitic rocks from northwestern Sardinia. Journal of Volcanology and Geothermal Research, **6**, pp. 375–389.

HELMSTAEDT, H., and TELLA, S. 1973. Pre-Carboniferous structural history of S.E. Cape Breton Island, Nova Scotia Maritime Sediments, **9**, pp. 88–99.

KELLEY, D. G., and MACKASEY, W. O. 1964. Basal Mississippian volcanic rocks in Cape Breton Island Geological Survey of Canada, Paper 64-34, 10 p.

KEPPIE, J. D., and DOSTAL, J. 1980. Paleozoic volcanic rocks of Nova Scotia. *In* The Caledonides in the U.S.A. *Edited by* D. R. Wones. Virginia Polytechnic Institute, Blacksburg VA, pp. 249–256.

KEPPIE, J. D., GILES, P. S., and BOEHNER, R. C. 1978*a*. Some Middle Devonian to Lower Carboniferous rocks of Cape George, Nova Scotia. Nova Scotia Department of Mines, Report 78-4, 12 p.

KEPPIE, J. D., DOSTAL, J., and ZENTILLI, M. 1978*b*. Petrology of the Early Silurian Dunn Point and McGillivray Brook Formations, Arisaig, Nova Scotia. Nova Scotia Department of Mines, Paper 78-5, 20 p.

LOCARDI, E. 1967. Uranium and thorium in the volcanic processes. Bulletin Volcanologique, **31**, pp. 235–260.

MAHOOD, G. A. 1981. A summary of the geology and petrology of the Sierra La Primavera, Salisco. Journal of Geophysical Research, **86**, pp. 10 137 – 10 152.

MURPHY, J. B. 1982. Tectonics and magmatism in the northern Antigonish Highlands. Ph.D. thesis, McGill University, Montreal, P.Q., 293 p.

MURPHY, J. B., KEPPIE, J. D., and HYNES, A. 1979. Geology of the northern Antigonish Highlands. Nova Scotia Department of Mines, Report 79-1, pp. 105–109.

ROGERS, J. J. W., and ADAMS, J. A. S. 1969*a*. Thorium. *In* Handbook of geochemistry. Vol. 2, No. 3. *Edited by* K. H. Wedepohl. Springer-Verlag, Berlin, pp. 90-B–90-O.

——— 1969*b*. Uranium. *In* Handbook of geochemistry. Vol. 2, No. 3. *Edited by* K. H. Wedepohl. Springer-Verlag, Berlin, pp. 92-B–92-O.

ROGERS, J. J. W., ADAMS, J. A. S., and GATLIN, B. 1965. Distribution of thorium, uranium and potassium concentrations in three cores from the Conway Granite, New Hampshire, U.S.A. American Journal of Science, **263**, pp. 817–822.

ROSHOLT, J. N., ZARTMAN, R. E., and NKOMO, I. T. 1973. Lead isotope systematics and uranium depletion in the Granite Mountains, Wyoming. Geological Society of America Bulletin, **84**, pp. 989–1002.

SARKAR, P. K. 1978. Petrology and geochemistry of the White Rock metavolcanic suite, Yarmouth, Nova Scotia. Ph.D. thesis, Dalhousie University, Halifax, N.S., 207 p.

SMITH, P. K., and MACDONALD, A. S. 1981. The Fisset Brook Formation at Lowland Cove, Inverness County, Nova Scotia. Nova Scotia Department of Mines and Energy Paper 81-1, 18 p.

SMITHERINGALE, W. G. 1973. Geology of parts of Digby, Bridgetown and Gaspereau Lake map-areas, Nova Scotia Geological Survey of Canada, Memoir 375, 78 p.

WINKLER, H. G. F., and VON PLATEN, H. 1961. Experimentelle Gesteinsmetamorphose. V. Experimentell anatektischer Schmelzen und ihre petrogenetische Bedeutung. Geochimica et Cosmochimica Acta, **24**, pp. 250–259.